

Effective interactions in the colloidal suspensions from HNC theory

Daniel Léger

*Laboratoire de Mécanique et d'Energétique Université de Valenciennes
et du Hainaut-Cambrésis Le Mont Houy,
59313 Valenciennes Cedex 9, France.**

Dominique Levesque ¹

*Laboratoire de Physique Théorique UMR CNRS 8627
Université Paris Sud Bâtiment 210, 91405 Orsay, France.†*

Abstract

The HNC Ornstein-Zernike integral equations are used to determine the properties of simple models of colloidal solutions where the colloids and ions are immersed in a solvent considered as a dielectric continuum and have a size ratio equal to 80 and a charge ratio varying between 1 and 4000. At an infinite dilution of colloids, the effective interactions between colloids and ions are determined for ionic concentrations ranging from 0.001 to 0.1 mol/l and compared to those derived from the Poisson-Boltzmann theory. At finite concentrations, we discuss on the basis of the HNC results the possibility of an unambiguous definition of the effective interactions between the colloidal molecules.

¹To whom correspondence should be addressed

PACS numbers: 61.20, 82.70Dd.

*Electronic address: daniel.leger@univ-valenciennes.fr

†Electronic address: dominique.levesque@th.u-psud.fr

I. INTRODUCTION

The large difference of sizes and electric charges between the colloids and molecules or atoms present in the colloidal suspensions is one of the main difficulties encountered in the theoretical study of these multicomponent solutions. A customary simplification is to approximate the solvent contributions to the solution properties by those of a dielectric continuum where are immersed the colloids and ions. From this simplification, it results that the colloidal suspensions are mixtures of colloids and ions where the coulombic interactions between charges are divided by the dielectric constant of the continuum. All excluded volume and polarization effects due to the solvent are neglected or assumed to increase notably the ion sizes by considering that the ions are surrounded with a shell of bound molecules of solvent, for instance a hydration shell. A new simplification is generally done since the colloids are considered as structureless, rigid, spherical and charged particles. With these approximations, the estimate of properties of colloidal suspensions is reduced to that of mixtures of spherical ions and particles where the size and charge of ions and particles have highly different values [1, 2, 3].

The screening effects which are present in the coulombic systems, lead to further simplify the description of the colloidal suspension by supposing that the interaction between colloidal particles due to their electric charges can be represented by an effective potential resulting from the screening of their own charges by the ions [1, 4, 5, 6]. The standard methods of liquid theory allow to avoid this latter approximation and to calculate the structural order and thermodynamic properties of the colloidal suspensions as those of mixtures of large charged particles and small ions. The main aim of this work is to demonstrate that the HNC Ornstein-Zernike (OZ) integral equations [7] allow to perform such a calculation for a size ratio between spherical colloidal particles and spherical ions equal to 80 and charge ratios ranging from 1 to 4000. Although these charge ratios are currently found in real suspensions, the size ratio is small compared to that characteristic of real colloids. However, a size ratio equal to 80 preserves the fact that the external surface of colloids is sufficiently large for allowing that the screening of the colloid charge by the ions is not hindered by excluded volume effects, because the external colloid surface is able to accommodate about 25000 small ions. Such a size ratio seems sufficient to perform a valuable comparison with the Poisson-Boltzmann (PB) theoretical approaches of the estimate of the effective interaction

between ions and colloids in the infinite dilution limit, in particular for values of the charge ratio larger than 1000.

In addition to the coulomb interactions, short range interactions of van der Waals type exist between the ions and colloids. These interactions will be also discarded in order to determine unambiguously the effective interactions induced solely by the interactions between the charges. The specific system studied is a neutral mixture of large charged hard spheres, the colloids, soluted in a fluid of one or two species of small charged hard spheres, the ions. The colloids are positively charged. A link between this model system and the real suspensions is made by attributing to the ions a hard core diameter of $\sigma_i = 5 \text{ \AA}$, a typical value for hydrated ions, giving for the colloid diameter a value of $\sigma_c = 400 \text{ \AA}$; this equivalence allows to express the ionic densities of the model in mol/l (M).

The numerical procedure used to solve the HNC integral equations is described in Section II, in the same section the results obtained at an infinite dilution of colloids are given and compared to those of the PB theory. In Section III we present the results obtained at finite concentration of the colloids. In the final Section, we summarize the results and discuss possible extensions of this work.

II. INFINITE DILUTION

To solve numerically the HNC OZ equations for symmetric and asymmetric mixtures of charged hard spheres, a sufficiently small integration step is needed to describe accurately the very steep peak existing at contact in the correlation functions between the negative ions and colloids [8, 9, 10, 11, 12, 13, 14]. Furthermore, the upper bound of the numerical integrations must be equal to several colloid diameters in order to study systems with a colloid finite concentration. Finally, at low ionic concentrations, the Debye length characterizing the screening effects can have a value of the same order than the colloid diameter which requires also the use of an upper bound of integration large enough to reach the asymptotic behavior of the correlation functions. With these constraints and the fact that the numerical solution of the HNC equations is obtained using a Fast Fourier transform algorithm, the numerical integrations are performed with $2^{18} = 262144 \Delta r$ or Δk steps in the r and k spaces. The colloid radius R_c , chosen as the unit of length, is equal to $16000 \Delta r$ and the ion radius to $200 \Delta r$. In r space, the integration upper bound is equal to $16.38 R_c$.

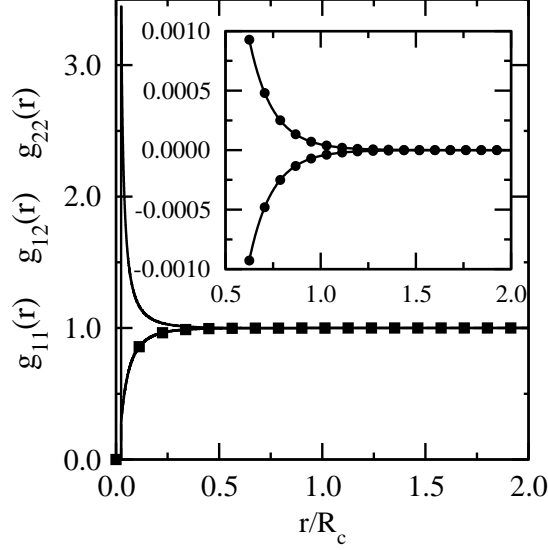


FIG. 1: Ion-ion correlation functions $g_{11}(r)$, $g_{12}(r)$ (solid lines) and $g_{22}(r)$ (filled squares) with $z_1 = -1$, $z_2 = 1$, $\rho_v = 0.01 M$ and $\rho_0 = 0$. Insert : fit of $g_{11}(r)$ and $g_{12}(r)$ (solid lines) by $A_{\alpha\beta} \exp(-\kappa_p r)/r$ (filled circles) ($\kappa_p R_c = 6.62$).

The coupling strength between charges is characterized by the Bjerrum length $l_B = e^2/\epsilon k_B T$ where ϵ is the dielectric constant of the solvent, e the electron charge, k_B the Boltzmann constant and T the temperature. For an aqueous suspension $l_B = 7.198 \text{ \AA}$ at $T = 293 \text{ K}$. The colloid and ion densities ρ_0 , ρ_1 and ρ_2 must be chosen in order to satisfy the electro-neutrality relation $z_0 \rho_0 + z_1 \rho_1 + z_2 \rho_2 = 0$ where z_0 , z_1 and z_2 are the colloid and ion charges.

In the solution of the HNC equations, the long range of the coulomb potential is taken into account by writing the direct correlation functions $c_{\alpha\beta}(r)$ ($\alpha, \beta = 0, 1$ and 2) :

$$c_{\alpha\beta}(r) = a_{\alpha\beta}(a_l, r) - l_B z_\alpha z_\beta \frac{u_l(a_l r)}{r} \quad (1)$$

where $u_l(a_l r) = \text{erf}(a_l r)$ and a_l is chosen equal to $0.9 R_c$. The functions $a_{\alpha\beta}(a_l, r)$ have a short range, because the asymptotic behavior of $c_{\alpha\beta}(r)$ at large r is equal to $-l_B z_\alpha z_\beta/r$.

The Fourier transform $\bar{f}(k)$ of a function $f(r)$ being defined by

$$\bar{f}(k) = 4\pi\rho \int_0^\infty \frac{\sin(kr)}{kr} f(r) r^2 dr \quad (2)$$

where $\rho = \rho_0 + \rho_1 + \rho_2$ (for an infinite dilution of colloids $\rho_0 = 0$), the Fourier transform of $u_l(a_l r)$ is $\bar{u}_l(k) = \exp(-k^2/(4 a_l^2))/k^2$ and that of $c_{\alpha\beta}(r)$

$$\bar{c}_{\alpha\beta}(k) = \bar{a}_{\alpha\beta}(k) - c_l \bar{u}_l(k) z_\alpha z_\beta. \quad (3)$$

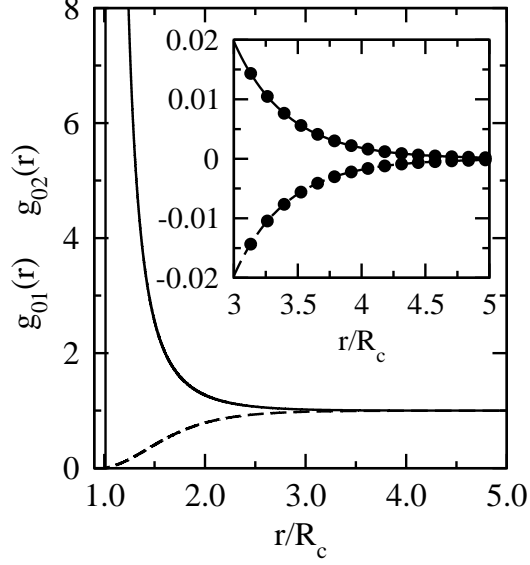


FIG. 2: Ion-colloid correlation functions $g_{01}(r)$ (solid line) and $g_{02}(r)$ (dashed line) with $z_1 = -1$, $z_2 = 1$, $\rho_v = 0.001 M$ and $\rho_0 = 0$. Insert : fit of $g_{01}(r)$ (solid line) and $g_{02}(r)$ (dashed line) by $A_{\alpha\beta} \exp(-\kappa_p r)/r$ (filled circles) ($\kappa_p R_c = 2.08$).

where $c_l = 4\pi\rho l_B$.

In k -space, the OZ equations at a colloidal infinite dilution write for the ion correlation functions

$$\begin{aligned}\bar{h}_{11}(k) &= \frac{\bar{c}_{11}(k) + x_2(\bar{c}_{12}^2(k) - \bar{c}_{11}(k)\bar{c}_{22}(k))}{\bar{D}_0(k)} \\ \bar{h}_{22}(k) &= \frac{\bar{c}_{22}(k) + x_1(\bar{c}_{12}^2(k) - \bar{c}_{11}(k)\bar{c}_{22}(k))}{\bar{D}_0(k)} \\ \bar{h}_{12}(k) &= \frac{\bar{c}_{12}(k)}{\bar{D}_0(k)}\end{aligned}\tag{4}$$

and the ion-colloid correlation functions

$$\begin{aligned}\bar{h}_{01}(k) &= \frac{\bar{c}_{01}(k)(1 - x_2\bar{c}_{22}(k)) + x_2\bar{c}_{12}(k)\bar{c}_{02}(k)}{\bar{D}_0(k)} \\ \bar{h}_{02}(k) &= \frac{\bar{c}_{02}(k)(1 - x_1\bar{c}_{11}(k)) + x_1\bar{c}_{12}(k)\bar{c}_{01}(k)}{\bar{D}_0(k)}\end{aligned}\tag{5}$$

where $x_1 = \rho_1/\rho$, $x_2 = \rho_2/\rho$ and

$$\bar{D}_0(k) = (1 - x_1\bar{c}_{11}(k))(1 - x_2\bar{c}_{22}(k)) - x_1x_2\bar{c}_{12}^2(k)\tag{6}$$

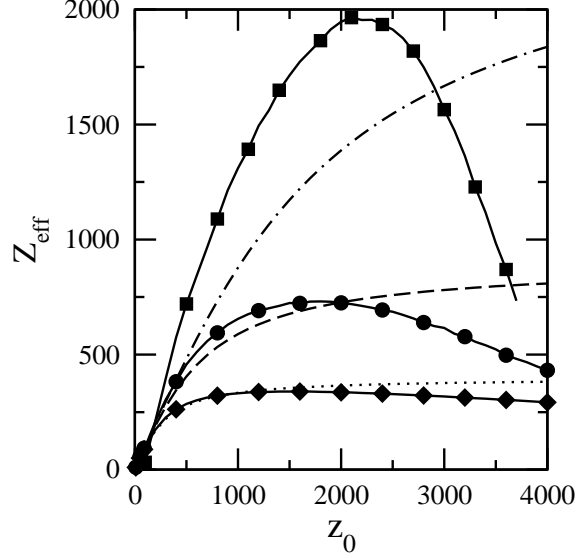


FIG. 3: At $\rho_0 = 0$, PB and HNC estimates of Z_{eff} versus z_0 for ionic charges $z_1 = -1$, $z_2 = 1$ at $\rho_v = 0.001$ M : PB dotted line, HNC solid line and filled diamonds, $\rho_v = 0.01$ M : PB dashed line, HNC solid line and filled circles and $\rho_v = 0.1$ M : PB dash-dotted line, HNC solid line and filled squares.

supplemented by the HNC closure in r -space :

$$\begin{aligned}
 h_{\alpha\beta}(r) &= g_{\alpha\beta}(r) - 1 \\
 &= \exp(-l_B z_\alpha z_\beta / r + h_{\alpha\beta}(r) - c_{\alpha\beta}(r)) - 1 \\
 &= \exp(-l_B z_\alpha z_\beta (1 - \text{erf}(a_l r)) / r) \\
 &\quad \times \exp(h_{\alpha\beta}(r) - a_{\alpha\beta}(a_l, r)) - 1.
 \end{aligned} \tag{7}$$

The convergence of the numerical solutions is obtained by using a Picard algorithm and considered to be achieved when the two successive iterations n and $n + 1$ of the functions $\gamma_{\alpha\beta}(r) = h_{\alpha\beta}(r) - a_{\alpha\beta}(a_l, r)$ satisfy the relations:

$$|\gamma_{\alpha\beta}^{(n+1)}(r) - \gamma_{\alpha\beta}^{(n)}(r)| < 10^{-6}. \tag{8}$$

In the literature, detailed comparisons of the two-body correlation functions and thermodynamic properties computed from the HNC theory and Monte-Carlo simulations have been made for ionic solutions [16, 17, 18, 19, 20, 21, 22, 23]. They have defined the domain of validity of the HNC approximation for ionic concentrations $\simeq 1$ M and charge and size ratios of the order of 1-20. These works have shown that the HNC closure gives an

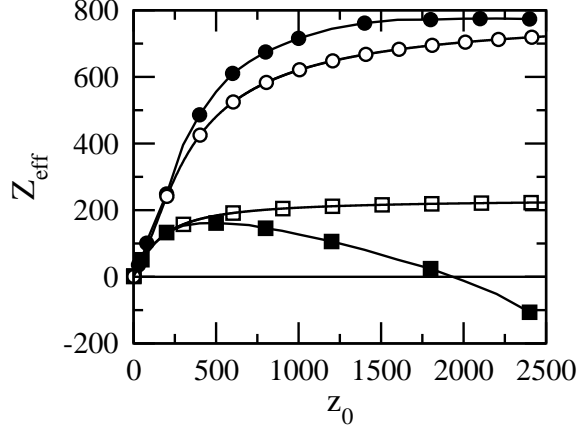


FIG. 4: At $\rho_0 = 0$, PB and HNC estimates of Z_{eff} versus z_0 at $\rho_v = 0.001$ M, ionic charges $z_1 = -1$, $z_2 = 2$: PB solid line and white circles, HNC solid line and filled circles, and $z_1 = -2$, $z_2 = 1$: PB solid line and white squares, HNC solid line and filled squares.

accurate description of the correlations at large r in symmetric or asymmetric systems of charged hard spheres, with equal or different diameters, immersed in a dielectric continuum. This satisfactory result constitutes a favorable basis to the study of the infinite dilution of colloids in our model. At $\rho_0 = 0$, the HNC equations (4) for the correlation functions of the small ions are independent of those giving the ion-colloid correlation functions $g_{01}(r)$ and $g_{02}(r)$ (cf. Eqs. (5)). Hence, it is possible to determine $g_{01}(r)$ and $g_{02}(r)$ at $\rho_0 = 0$ for any charge z_0 when the equations (4) have been solved. Such a computation has been realized for $z_0 < 4000$ and symmetric ($z_1 = -1$, $z_2 = 1$) or asymmetric ($z_1 = -2$, $z_2 = 1$) and ($z_1 = -1$, $z_2 = 2$) ionic solutions where the densities ρ_v of the ionic species with the highest valence, are equal to 0.1, 0.01 and 0.001 M (i.e. $\rho_v \sigma_i^3 = 0.007528$, 0.0007528 and 0.00007528), respectively.

From the correlation functions, there are several possible definitions of the effective interactions between colloids or more generally between specified components of a multi-component mixture [2, 5]. One of those is the potential of mean force $v_{\alpha\beta}^m(r)$ given by $\log\{g_{\alpha\beta}(r)\} = -\beta v_{\alpha\beta}^m(r)$. Theoretical approaches, such as the DLVO theory [1, 4], provide an explicit form for the effective interaction between colloids :

$$\beta v_{00}^{eff}(r) = Z_{eff}^2 l_B \left[\frac{\exp(\kappa_D R_c)}{1 + \kappa_D R_c} \right]^2 \frac{\exp(-\kappa_D r)}{r} \quad (9)$$

where κ_D is the inverse Debye length defined by $\kappa_D^2 = 4\pi l_B (z_1^2 \rho_1 + z_2^2 \rho_2)$, and the parameter

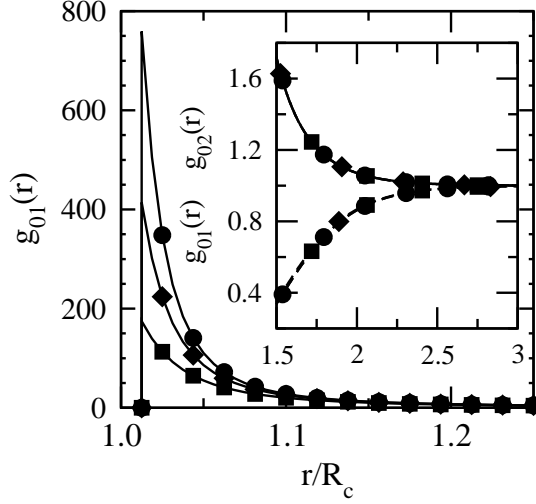


FIG. 5: At $\rho_0 = 0$, $\rho_v = 0.001$ M and ionic charges $z_1 = -1$, $z_2 = 2$, variation of the functions $g_{01}(r)$ near $r \simeq R_c$: $z_0 = 1200$ solid line and filled squares, $z_0 = 1800$ solid line and filled diamonds, $z_0 = 2400$ solid line and filled circles. Insert : for $1.5R_c < r < 3R_c$, $g_{01}(r)$ (solid line and filled squares $z_0 = 1200$, diamonds $z_0 = 1800$ and circles $z_0 = 2400$) and $g_{02}(r)$ (dashed line and filled squares $z_0 = 1200$, diamonds $z_0 = 1800$ and circles $z_0 = 2400$).

Z_{eff} is conventionally called the effective charge of the colloids.

In the limit $\rho_0 = 0$, from the linearized PB theory, a similar expression is obtained for the effective interaction between colloid and ions

$$\beta v_{0\alpha}^{eff}(r) = Z_{eff} z_\alpha l_B \frac{\exp(\kappa_D R_c)}{(1 + \kappa_D R_c)} \frac{\exp(-\kappa_D r)}{r} \quad (10)$$

where $\alpha = 1$ or 2 . For symmetric and asymmetric ionic solutions, without colloids, the PB theory also predicts that, at large r , the effective interactions between the ions are Yukawa potentials similar to $v_{0\alpha}^{eff}(r)$. This result, for instance, has been verified by computing $v_{\alpha\beta}^m(r)$ from the correlation functions $g_{\alpha\beta}(r)$ determined by MC simulations for systems of charged hard spheres with equal diameters and densities of ~ 1 M [22]. Similarly, an analytical expression of $v_{\alpha\beta}^m(r)$, with the same functional dependence at large r as $v_{0\alpha}^{eff}$, will be found from the correlation functions computed from the HNC OZ equations (4) and (5), when the singularity nearest to the real axis of the function $1/\bar{D}_0(k)$ is a simple pole located at $k = i\kappa_p$ [24, 25].

Numerical methods have been derived for the determination of the zeros of $\bar{D}_0(k)$ for complex values of k [26, 27, 28, 29, 30]. They need the calculation of integrals having the

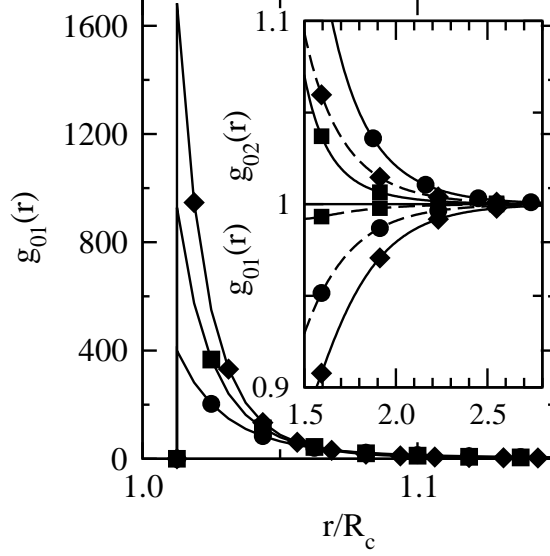


FIG. 6: At $\rho_0 = 0$, $\rho_v = 0.001$ M and ionic charges $z_1 = -2$, $z_2 = 1$, variation of the functions $g_{01}(r)$ near $r \simeq R_c$: $z_0 = 1200$ solid line and filled circles, $z_0 = 1800$ solid line and filled squares, $z_0 = 2400$ solid line and filled diamonds. Insert: for $1.5R_c < r < 3R_c$, $g_{01}(r)$ (solid line and filled circles $z_0 = 1200$, squares $z_0 = 1800$ and diamonds $z_0 = 2400$) and $g_{02}(r)$ (dashed line and filled circles $z_0 = 1200$, squares $z_0 = 1800$ and diamonds $z_0 = 2400$).

typical expression

$$I_p(k_0, k_1) = 4\pi \int_0^\infty r^2 c_{\alpha,\beta}^{sr}(r) \sinh(k_0 r) \cos(k_1 r) dr \quad (11)$$

where $c_{\alpha,\beta}^{sr}(r) = c_{\alpha,\beta}(r) + l_B z_a z_b / r$ and k_1 and k_0 are the real and imaginary parts of k . In practice, such integrals are not easily estimated when the upper limit of the numerical integration on r is ~ 500 times the radius of the ions.

This calculation requires at least an accuracy of the order of $10^{-8} - 10^{-10}$ on the $c_{\alpha,\beta}^{sr}(r)$ functions at large r which is not achieved with the present scheme used to solve the OZ equations. Therefore, we analyse the asymptotic behaviors of the $g_{\alpha,\beta}(r)$ at infinite dilution by supposing that the pole of $1/\bar{D}_0(k)$, closest to the real axis, is effectively on the imaginary axis. With this hypothesis, $\beta v_{\alpha,\beta}^m(r)$ should be equal to $A_{\alpha,\beta} \exp(-\kappa_p r)/r$ with κ_p identical for all the functions $v_{\alpha,\beta}^m(r)$. The determination of $A_{\alpha,\beta}$ and κ_p is obtained from a fit of $\log\{g_{\alpha,\beta}(r)\}$ by $A_{\alpha,\beta} \exp(-\kappa_p r)/r$, for r sufficiently large. However, the domains of large r values where the functions $|\log\{g_{\alpha,\beta}(r)\}|$ are smaller than 10^{-6} must be excluded due to the numerical uncertainties on the solutions of the OZ equations. The domains of r values, used

in the fits, correspond to the distances for which $10^{-4} < |\log\{g_{\alpha\beta}(r)\}| < 10^{-1}$ where the numerical uncertainties are two orders of magnitude smaller than the values of the fitted functions.

Examples of curve fittings of $\log\{g_{\alpha\beta}(r)\}$ are given in Figs. 1 and 2 ; these figures show unambiguously that these functions are accurately described by the presupposed analytical form $A_{\alpha\beta} \exp(-\kappa_p r)/r$. For a given ionic density, the values of κ_p obtained from the curve fitting of the functions $\log\{g_{01}(r)\}$ and $\log\{g_{02}(r)\}$ are independent of z_0 when the values of z_0 vary from 1 to 4000 and identical to those determined by the fit of $\log\{g_{11}(r)\}$, $\log\{g_{12}(r)\}$ and $\log\{g_{22}(r)\}$. At $\rho_v = 0.1, 0.01$ and 0.001 and ionic charges $(z_1 = -1, z_2 = 1)$, $(z_1 = -2, z_2 = 1)$ and $(z_1 = -1, z_2 = 2)$, the values for κ_p differ by a few percent from κ_D computed for the same ionic concentrations and charges. At these weak packing fractions of the ions, the differences between κ_p and κ_D result from contributions associated with the finite ionic density, κ_p being expected to be equal to κ_D only in the limit of very low densities where the functions $c_{\alpha,\beta}^{sr}(r)$ go to zero.

In the HNC theory, the description of $g_{01}(r)$ and $g_{02}(r)$ at large r by a Yukawa function is in agreement with the expressions of the PB theory for the effective interactions between ions and colloids at infinite dilution. It is thus possible to compare the values of the parameter Z_{eff} recently computed from PB theory with those deduced from the values of the parameters A_{01} and A_{02} by writing $A_{0\alpha}$ in a form identical to that derived from PB theory :

$$A_{0\alpha} = Z_{eff}^{HNC} z_{\alpha} l_B \frac{\exp(\kappa_p R_c)}{(1 + \kappa_p R_c)}. \quad (12)$$

Obviously, this expression does not result from a boundary condition similar to that satisfied by the solution of the PB equation on the colloid surface and can be considered as a definition of Z_{eff}^{HNC} . The possibility to write $A_{0\alpha}$ in such a form is partly confirmed by the fact that $A_{01}/A_{02} = z_1/z_2$ within the limits of the accuracy of the fit.

Recently PB expressions of Z_{eff} have been derived. The most simple expression [31], valid in the limit z_0 and $R_c/\sigma_i \rightarrow \infty$, is

$$Z_{eff}^a = \frac{4R_c}{l_B} (1 + \kappa_D R_c). \quad (13)$$

An expression, a priori valid for all values of z_0 and R_c when, at infinite dilution, the colloids are immersed in low density ionic solutions of monovalent ions, has been derived

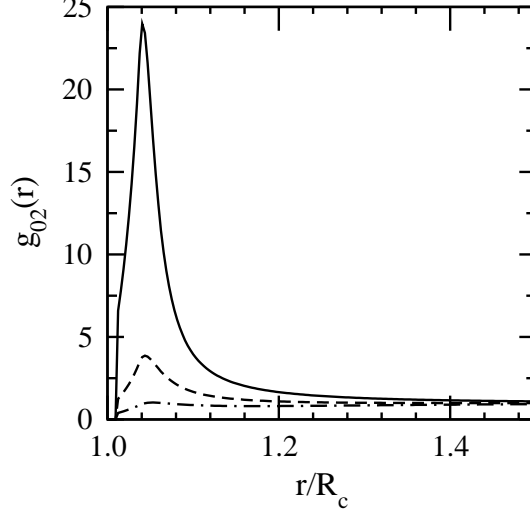


FIG. 7: At $\rho_0 = 0$, $\rho_v = 0.001$ M and ionic charges $z_1 = -2$, $z_2 = 1$, variation of the functions $g_{02}(r)$ near $r \simeq R_c$: $z_0 = 1200$ dash-dotted line, $z_0 = 1800$ dashed line, $z_0 = 2400$ solid line.

[32] by using the asymptotically exact solution of the PB equation [33]

$$Z_{eff}^b = \frac{4R_c^2}{l_B} t(x) + \frac{4R_c}{l_B} \left(5 - \frac{t^4(x) + 3}{t^2(x) + 1} \right) t(x). \quad (14)$$

where $x = z_0 l_B / (R_c (2\kappa_D R_c + 2))$ and $t(x) = (\sqrt{1+x^2} - 1)/x$. This derivation has been recently extended to the cases of ion mixtures with asymmetric charges $z_1 = -2$, $z_2 = 1$ and $z_1 = -1$, $z_2 = 2$ [34]. It gives $Z_{eff}^c = z_0 f(x)$ where $f(x)$ is an intricate function of $x = z_0 l_B / \kappa_D R_c^2$, depending on the charge asymmetry of the ions. The main results of these theoretical estimates are that, for $z_0 = 1 - 100$, $Z_{eff} \simeq z_0$ and, for $z_0 > 1000$, Z_{eff} goes to a constant value of the order of Z_{eff}^a .

From the fits of the functions $\log\{g_{\alpha\beta}(r)\}$, similar in accuracy to those plotted in Figs. 1 and 2, we have computed the values of κ_p and Z_{eff}^{HNC} resulting from the HNC OZ theory (cf. Eq. (12)). At $\rho_v = 0.001$ M, $\kappa_p R_c$ and $\kappa_D R_c$ are respectively equal to 2.089 and 2.087, at $\rho_v = 0.01$ M equal to 6.62 and 6.60, and at $\rho_v = 0.1$ they differ by 5% and are equal to 21.8 and 20.8. Fig. 2 shows that for $r > 2R_c$, $g_{01}(r)$ and $g_{02}(r)$ are symmetric with respect to 1, and Fig. 3 that the PB and HNC estimates Z_{eff}^b and Z_{eff}^{HNC} are in good agreement at the ionic concentrations of 0.001 and 0.01 M when $z_0 < 2000$, in particular the two estimates reach a maximal value near $z_0 \simeq 2000$. For larger values of z_0 the PB and HNC estimates Z_{eff}^b and Z_{eff}^{HNC} differ systematically: Z_{eff}^b stays constant whereas Z_{eff}^{HNC} decreases.

At $\rho_v = 0.1$ M, in the considered range of z_0 , the PB values of Z_{eff} do not reach their

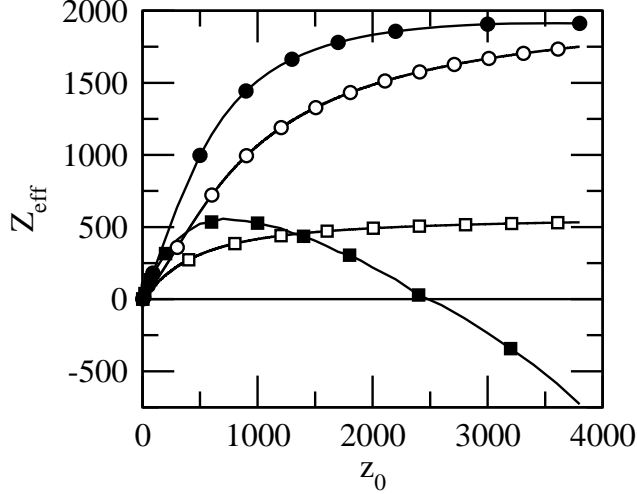


FIG. 8: At $\rho_0 = 0$, PB and HNC estimates of Z_{eff} versus z_0 for ionic concentrations $\rho_v = 0.01$ M, ionic charges $z_1 = -1$, $z_2 = 2$: solid line and white circles PB, solid line and filled circles HNC, and $z_1 = -2$, $z_2 = 1$: solid line and white squares PB, solid line and filled squares HNC.

asymptotic value. The HNC estimates of Z_{eff} would have values exceeding largely z_0 if Z_{eff}^{HNC} was calculated from Eq. (12) by using κ_D and not κ_p . This result seems to be an indication that the finite concentration effects of co-ions and counter-ions cannot be neglected when the ionic concentrations are of the order of or larger than 0.1 M.

For the charge asymmetric ionic mixtures of $\rho_v = 0.001$ M, $z_1 = -2$, $z_2 = 1$ and $z_1 = -1$, $z_2 = 2$, Fig. 4 presents a comparison between Z_{eff}^c and Z_{eff}^{HNC} . For the case $z_1 = -1$, $z_2 = 2$, the qualitative agreement is excellent and the quantitative difference is not larger than 10%. The two estimates of Z_{eff} are almost constant when $z_0 > 1000$. Fig. 5 shows that, in agreement with the fact that Z_{eff}^{HNC} is quasi constant for these values of z_0 , $g_{01}(r)$ and $g_{02}(r)$ vary only near $r \simeq R_c$ and stay almost unchanged when $r > 2R_c$. In the case $z_1 = -2$, $z_2 = 1$, Z_{eff}^c and Z_{eff}^{HNC} differ for $z_0 > 500$, Z_{eff}^c is constant but Z_{eff}^{HNC} decreases and becomes negative near $z_0 = 1800$. Fig. 6 shows the variation of $g_{01}(r)$ and $g_{02}(r)$ which, taking into account the ratio z_1/z_2 and the sign inversion of Z_{eff}^{HNC} , retain the correct symmetry with respect to 1 when $r > 2R_c$.

For $r < 2R_c$, the main feature is the appearance of a peak in $g_{02}(r)$ (cf. Fig. 7) near $r \simeq R_c + 1.5\sigma_i$ characterizing an overscreening of the colloid charge for large z_0 by the negative ions which allows the positive ions to be located close to the colloid surface. This overscreening seems to be at the origin the sign inversion of the colloid-ion potential of mean

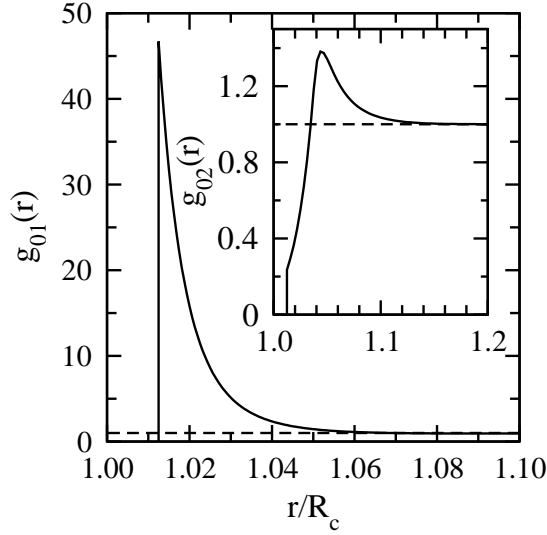


FIG. 9: At $\rho_0 = 0$, $\rho_v = 0.1$ M $z_1 = -2$, $z_2 = 1$ and $z_0 = 3800$: ion-colloid correlation functions $g_{01}(r)$ and $g_{02}(r)$.

force, which is not obtained in the PB theory.

A similar behavior is found for $\rho_v = 0.01$ as shown by the comparison between Z_{eff}^c and Z_{eff}^{HNC} presented in Fig. 8. At $\rho_v = 0.1$, $z_1 = -2$, $z_2 = 1$ ($\kappa_p R_c > 25$), Fig. 9 shows that $g_{02}(r)$ exhibits a peak at $r \simeq R_c + 1.5\sigma_i$ for $z_0 = 3800$ which indicates an overscreening of the colloid charge. However the large value of $\kappa_p R_c$ implies a very steep decrease of the correlation functions and the range of r values where a significant fit of $g_{01}(r)$ and $g_{02}(r)$ is possible, is very small ($\simeq 0.1R_c$) and does not allow for an estimate of Z_{eff}^{HNC} .

III. FINITE CONCENTRATION

The *binary* mixture composed of colloids and counterions with $z_1 = -1$, without added salt, has been well studied in the literature [8, 12] and we briefly present and discuss the HNC results obtained for the case of a colloid-counterion size ratio equal to 80 at a colloid packing fraction $\eta_c = \pi\rho_c\sigma_c^3/6 = 0.1$. For this mixture, a numerical solution of the HNC OZ equations is only found when $z_0 < 130$. This limitation on the z_0 values is similar to that obtained in Refs. [12, 13, 15]. At $z_0 = 130$, using the previously adopted values of ion and colloid radii, the ionic concentration is $\simeq 0.0064$ M and the ionic packing fraction $\simeq 0.0000253$. Even at low values of z_0 the asymptotic behavior of the three correlation functions corresponds

TABLE I: Colloid packing fraction : η_c , density of the ion species with the highest valence : ρ_v , ion charges : z_1 and z_2 , maximum colloid charge : z_0^{\max} , κ_D and κ_D^c : inverse screening Debye length without and with the colloid charge contribution. The last line corresponds to a binary ion-colloid mixture.

η_c	$\rho_v M$	z_1	z_2	z_0^{\max}	$\kappa_D R_c$	$\kappa_D^c R_c$
0.0001	0.001	-1	1	450	2.09	2.10
0.0001	0.001	-2	1	270	2.55	2.55
0.0001	0.001	-1	2	630	3.61	3.61
0.001	0.001	-1	1	300	2.09	2.10
0.001	0.001	-2	1	260	2.57	2.57
0.001	0.001	-1	2	465	3.62	3.62
0.01	0.001	-2	1	189	2.67	2.67
0.1	0.003	-1	1	109	2.35	2.59
0.1		-1		130		1.67

to damped oscillations (cf. Fig. 10) indicating that, in the OZ equations (cf. Eq. (4)), the asymptotic behavior is determined by poles of $1/\bar{D}_0(k)$ symmetric with respect to the imaginary axis. A fit of the pair correlation functions at $z_0 = 130$ for $8R_c < r < 25R_c$ (cf. above and below for a detailed discussion of the fitting procedure) shows that these functions oscillate with the same period equal to $1.95R_c$ (cf. Fig 11) and have the same damping constant $\kappa_p R_c = 0.24$ about 6 times smaller than the inverse screening Debye length $\kappa_D R_c = 1.67$ (cf. Table 1).

In Fig. 10, it is seen from $g_{01}(r)$ that the screening of the colloid charges occurs over a distance which varies between 1.5 and 0.6 R_c when z_0 increases from 1 to 130. For these values of z_0 , the range of the screening effects stays sufficiently large so that the coulombic repulsion shifts the main peak of $g_{00}(r)$ from $2R_c$ to $3.8R_c$. This displacement induces a reinforcement of the excluded volume effects between the colloids. For $z_0 \simeq 50 - 130$, $g_{00}(r)$ has the typical form of the pair correlation function of a dense monoatomic fluid. It seems, although difficult to establish numerically, that this increase of the excluded volume effects is the main cause of the instability of the HNC OZ equations at $z_0 > 130$.

The *ternary* solutions of colloids, positive and negative ions have been considered for

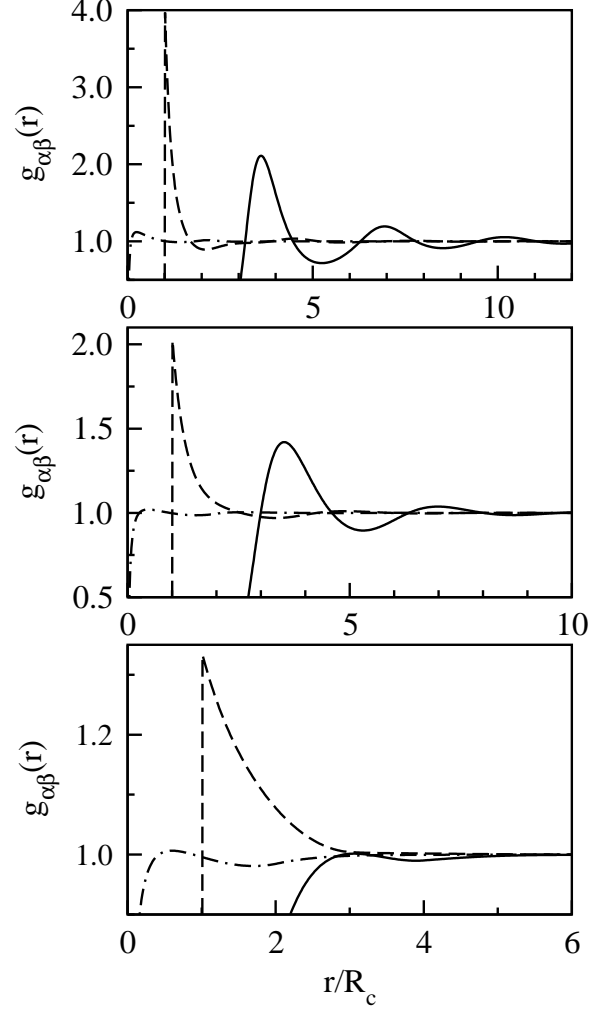


FIG. 10: At $\eta_c = 0.1$, $\rho_2 = 0$ and $z_1 = -1$ colloid-colloid $g_{00}(r)$ (solid line), ion-colloid $g_{01}(r)$ (dashed line) and ion-ion $g_{11}(r)$ (dash-dotted line) correlation functions, from bottom to top $z_0 = 10$, $z_0 = 50$ and $z_0 = 130$.

different colloid packing fractions, ionic concentrations and colloid charges summarized in Table 1. In these mixtures for given densities of the colloids and the positive ions, the density of the negative ions is fixed by the electroneutrality condition. In Table 1, z_0^{max} denotes the maximum value of z_0 at which the HNC equations can be solved by using the previously described numerical iterative scheme. In the mixtures, the asymptotic behaviors of the correlation functions $g_{\alpha\beta}(r)$ can be analysed similarly to the infinite dilution case, since a typical OZ equation for a correlation function has the form

$$\bar{h}_{01}(k) = \frac{(\bar{c}_{01}(k) + x_2 \bar{c}_{02}(k) \bar{c}_{12}(k) - x_2 \bar{c}_{22}(k) \bar{c}_{01}(k))}{\bar{D}(k)} \quad (15)$$

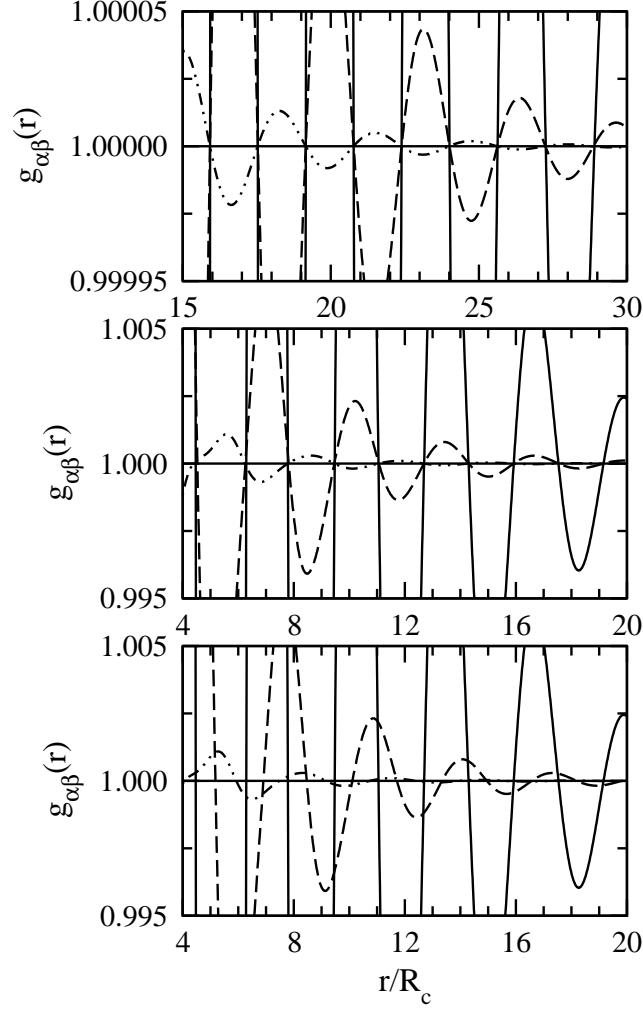


FIG. 11: At $\eta_c = 0.1$, $\rho_2 = 0$, $z_1 = -1$ and $z_0 = 130$, : colloid-colloid $g_{00}(r)$ (solid line), ion-colloid $g_{01}(r)$ (dashed line) and ion-ion $g_{11}(r)$ (dash-dotted line) correlation functions. From bottom to top : $g_{00}(r)$, $g_{01}(r)$ and $g_{11}(r)$, and, after an appropriated shift of $g_{01}(r)$ and $g_{11}(r)$ on r equal to d_{01}^p and d_{02}^p (cf. Eq. [17]), for $4 < r/R_c < 20$ and $15 < r/R_c < 30$ close views showing the identity of the oscillation period of the three correlation functions (the maxima and minima of the oscillations of $g_{00}(r)$ and $g_{01}(r)$ can be truncated).

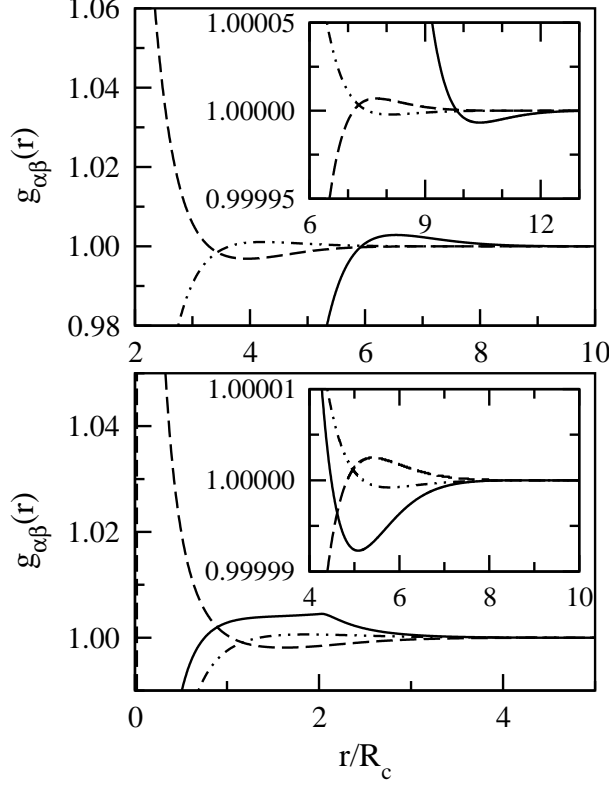


FIG. 12: At $\eta_c = 0.001$, $z_1 = -1$, $z_2 = 1$, $\rho_v = 0.001$ M and $z_0 = 300$, *bottom* : correlation functions $g_{11}(r)$ (solid line), $g_{12}(r)$ (dashed line) and $g_{22}(r)$ (dash-dotted line), insert : close view for $r > 4R_c$, and *top* : $g_{00}(r)$ (solid line), $g_{01}(r)$ (dashed line) and $g_{02}(r)$ (dash-dotted line), insert : close view for $r > 6R_c$.

where the expression of $\bar{D}(k)$, identical for all $\bar{h}_{\alpha\beta}(k)$, is

$$\begin{aligned}
\bar{D}(k) = & (1 - x_2 \bar{c}_{22}(k) - x_1 \bar{c}_{11}(k) - x_0 \bar{c}_{00}(k) \\
& + x_1 x_2 \bar{c}_{11}(k) \bar{c}_{22}(k) - x_1 x_2 \bar{c}_{12}(k)^2 \\
& - x_0 x_1 \bar{c}_{01}(k)^2 - x_0 x_2 \bar{c}_{02}(k)^2 \\
& + x_0 x_1 \bar{c}_{11}(k) \bar{c}_{00}(k) - x_0 x_1 x_2 \bar{c}_{11}(k) \bar{c}_{00}(k) \bar{c}_{22}(k) \\
& + x_0 x_1 x_2 \bar{c}_{11}(k) \bar{c}_{02}(k)^2 \\
& - 2 x_0 x_1 x_2 \bar{c}_{01}(k) \bar{c}_{12}(k) \bar{c}_{02}(k) \\
& + x_0 x_2 \bar{c}_{00}(k) \bar{c}_{22}(k) + x_0 x_1 x_2 \bar{c}_{01}(k)^2 \bar{c}_{22}(k) \\
& + x_0 x_1 x_2 \bar{c}_{12}(k)^2 \bar{c}_{00}(k))
\end{aligned} \tag{16}$$

where $x_0 = \rho_0/\rho$.

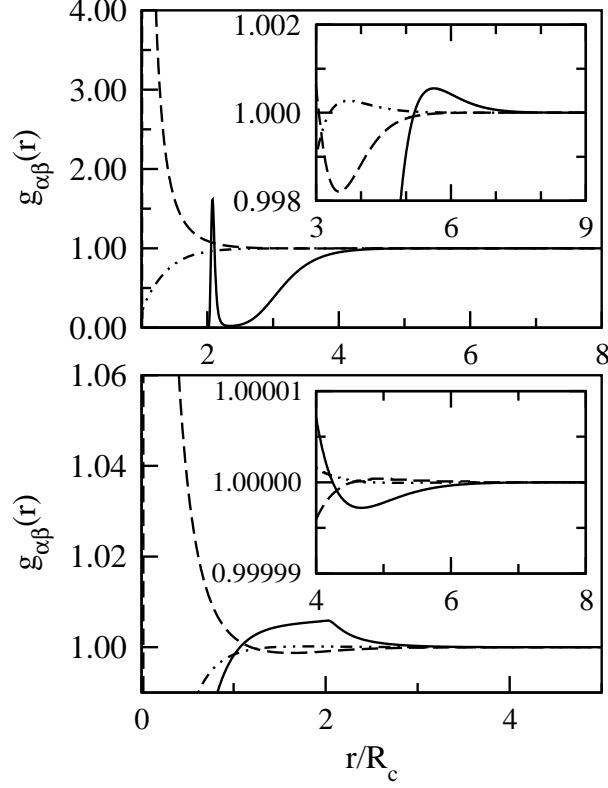


FIG. 13: At $\eta_c = 0.001$, $z_1 = -2$, $z_2 = 1$, $\rho_v = 0.001$ M and $z_0 = 259$, *bottom* : correlation functions $g_{11}(r)$ (solid line), $g_{12}(r)$ (dashed line) and $g_{22}(r)$ (dash-dotted line), insert : close view for $r > 4R_c$, and *top* : $g_{00}(r)$ (solid line), $g_{01}(r)$ (dashed line) and $g_{02}(r)$ (dash-dotted line), insert : close view for $r > 3R_c$ (the scale of y -axis precludes to identify the maxima and minima for $r > 6R_c$).

Clearly, the zeros of $\bar{D}(k)$, if they exist at complex values of k near the real axis, determine the decrease of all the functions $g_{\alpha\beta}(r)$. Since these functions are real, the most simple locations of these zeros correspond to values of k on the imaginary axis, $k = i\kappa_p$, giving at large r an exponential decrease of $g_{\alpha\beta}(r) \simeq 1 + A_{\alpha\beta} \exp(-\kappa_p r)/r$, or to values of k symmetric with respect to the imaginary axis, $k = k_0 + i\kappa_p$ and $k = -k_0 + i\kappa_p$, giving an oscillatory exponential damped decrease of $g_{\alpha\beta}(r) \simeq 1 + A_{\alpha\beta} \exp(-\kappa_p r) \cos(k_0 r + d_{\alpha\beta})/r$. In the first case, at large r all correlation functions are exponentially decreasing, in the second case all the functions $g_{\alpha\beta}(r)$ oscillate with an identical period and damping. Contrary, to the infinite dilution case where, for the considered ionic solutions, an exponential decrease was always obtained, both exponential and oscillatory damped decreases are found for finite colloid concentrations.

For instance, in the case of a symmetric ionic solution ($z_1 = -1$, $z_2 = 1$), at $\rho_v = 0.001\text{M}$ and $\eta_c = 0.001$, the OZ equations can be solved in the domain $1 < z_0 < 300$. For $z_0 < 100$, $g_{00}(r)$ increases monotonically from 0, at short distance, towards 1 at large r . Above this value of z_0 (cf. Fig. 12), $g_{00}(r)$ presents, at $r \simeq 6 - 7R_c$, a weak broad peak, larger than 1, then, at $r \simeq 10R_c$, a minimum smaller than 1, and finally, at large r , increases monotonically towards 1. A similar behavior is obtained for $g_{11}(r)$; the peak and minimum, which exist also for $z_0 > 100$, are located at $r \simeq 1 - 2R_c$ and at $r \simeq 5 - 6R_c$, respectively. At larger r , $g_{11}(r)$ increases monotonically towards 1. The function $g_{22}(r)$, different from $g_{11}(r)$ due to the finite density of the colloids, presents a peak and minimum for $z_0 > 100$ and a final monotonic increase towards 1 at large r . The function $g_{12}(r)$, has a peak near $r = \sigma_i$, obviously due to the attraction between ions of opposite charges. For $r > 1.5R_c$ and $z_0 > 100$, the monotonic decrease of this peak towards 1 is modified, $g_{12}(r)$ has a minimum, smaller than 1, at $r \simeq 2 - 3R_c$, followed by a local maximum at $r = 5R_c$, and for larger r decreases monotonically towards 1.

The functions $g_{01}(r)$ and $g_{02}(r)$ when $z_0 < 100$ have the expected behavior at large r characterized, respectively, by a monotonic decrease for $g_{01}(r)$ and increase for $g_{02}(r)$ towards 1. But, above $z_0 > 100$, $g_{01}(r)$ ($g_{02}(r)$) has, a local minimum (maximum) at $r \simeq 4R_c$, followed at $r \simeq 7R_c$ by a local maximum (minimum) and at large r decreases (increases) towards 1.

In summary, for low values of z_0 , the asymptotic behavior of the correlation functions seems exponential, as in the case of infinite dilution of the colloids. For a large value of z_0 , it presents oscillations, although, within the limit of numerical accuracy, only one or two oscillations can be observed unambiguously.

When $z_1 = -2$ and $z_2 = 1$ or $z_1 = -1$ and $z_2 = 2$, similar analysis of the asymptotic behavior of the correlation functions can be made with identical conclusions, since in these cases, the HNC equations can be solved for $z_0 < 260$ and $z_0 < 465$, respectively (cf. Table 1). The main remark concerns the system with $z_1 = -2$ and $z_2 = 1$, where the onset of a peak in $g_{00}(r)$ at $r \simeq 2.08R_c$ for $z_0 > 250$, indicates that the screening of the colloid charges by negative ions has a range sufficiently short for two colloids to be separated by a distance of one or a few ion diameters (cf. Fig. 13).

At the packing fraction $\eta_c = 0.0001$ and $\rho_v = 0.001\text{ M}$, the HNC equations can be solved numerically for symmetric ($z_1 = -1$ and $z_2 = 1$) and asymmetric ($z_1 = -1$ and $z_2 = 2$,

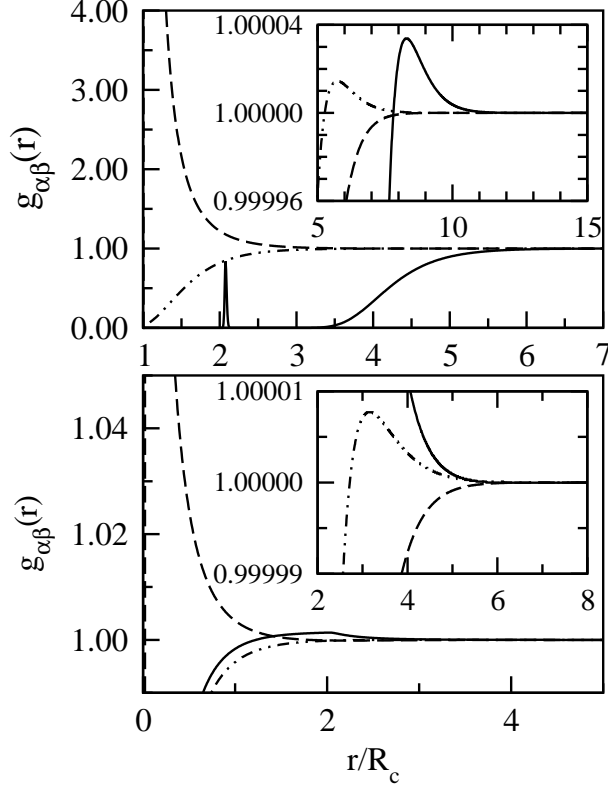


FIG. 14: At $\eta_c = 0.0001$, $z_1 = -1$, $z_2 = 1$, $\rho_v = 0.001$ M and $z_0 = 460$, *bottom* : correlation functions $g_{11}(r)$ (solid line), $g_{12}(r)$ (dashed line) and $g_{22}(r)$ (dash-dotted line), insert : close view for $r > 2R_c$, and *top* : $g_{00}(r)$ (solid line), $g_{01}(r)$ (dashed line) and $g_{02}(r)$ (dash-dotted line), insert : close view for $r > 5R_c$.

$z_1 = -2$ and $z_2 = 1$) ions up to $z_0 < 460$, $z_0 < 630$ and $z_0 < 270$, respectively. The main difference, compared to the case of the colloid packing fraction of $\eta_c = 0.001$, is that, for $z_0 > 100$, a peak or minimum appears at $r > 2R_c$ in the ion-ion correlation functions and at $r > 4R_c$ or $r > 6R_c$ in the ion-colloid or colloid-colloid correlation functions. Beyond this peak or minimum, the correlation functions go monotonically towards 1 within the numerical accuracy of the HNC solutions. For the three considered cases of ionic charges, near z_0^{max} , a peak appears in $g_{00}(r)$ for $r \simeq 2.08R_c$, indicating that the screening of the colloid charges allows a close approach between colloids (cf. Fig. 14).

In the other studied mixtures at $\eta_c = 0.01$, and $\eta_c = 0.1$ with symmetric and asymmetric ionic charges, the correlation functions have asymptotic behaviors qualitatively similar to those found for lower colloid packing fractions. The main quantitative difference is that the non-monotonic decay of the correlations appears at low colloid charges $z_0 \simeq 10$. For the

colloid packing fraction $\eta_c = 0.1$, the correlation functions have an oscillatory behavior at large r for $z_0 > 20$. At this value of η_c and $z_0 > 70 - 80$, several oscillations can be identified at large r with amplitudes larger than the numerical error.

From the results obtained at a finite density of the colloids, it appears that the asymptotic behavior of the correlations functions, as computed from the HNC OZ equations, is compatible with the hypothesis that it is determined by the poles of $1/\bar{D}(k)$ as only monotonic or oscillatory behaviors have been found. It is worth remarking that, since the type of asymptotic decrease is the same for all the correlation functions, it should be sufficient to consider only one of the correlation functions for determining this behavior, for instance $g_{00}(r)$. However, as in the case of the infinite dilution colloid system, such a determination, due to the present numerical accuracy on $g_{00}(r)$ can be performed only in the range of r for which $|g_{00}(r) - 1| > 10^{-6}$. A similar remark obviously applies to all the other correlations functions. With the hypothesis that the asymptotic behavior of the functions $g_{\alpha\beta}(r)$ is determined by simple poles near the real axis, and considering only the two nearest poles to the real axis, a function $g_{\alpha\beta}(r)$ writes [22, 24, 25]

$$g_{\alpha\beta}(r) \simeq 1 + A_{\alpha\beta}^p \exp(-\kappa_p r) \cos(k_p^0 r + d_{\alpha\beta}^p)/r + A_{\alpha\beta}^o \exp(-\kappa_o r) \cos(k_o^0 r + d_{\alpha\beta}^o)/r. \quad (17)$$

The relative values of κ_p and κ_o determine the dominant contribution to the asymptotic behavior. When, for instance, $\kappa_p \ll \kappa_o$, and k_p^0 and $d_{\alpha\beta}^p$ equal to or different from zero, the decrease at large r is exponential or damped oscillatory ; when $\kappa_p \simeq \kappa_o$, obviously the type of decrease can be difficult to identify from the numerical values of $g_{\alpha\beta}(r)$, in particular when $A_{\alpha\beta}^p \ll A_{\alpha\beta}^o$. Figure 15 shows the behavior of the functions $g_{\alpha\beta}(r)$ for the suspensions with $\eta_c = 0.1$, $z_0 = 108$, $z_1 = -1$, $z_2 = 1$ and $\rho_v = 0.003M$. All functions present damped oscillations for $r > 6R_c$, in particular, $g_{00}(r)$ which is above the level of numerical uncertainties until $r \simeq 15R_c$. This result indicates that, assuming $\kappa_p < \kappa_o$ and a value of A_{00}^p estimated from Eq. (12), the asymptotic behavior of $g_{00}(r)$ is not determined by the Debye screening since for $r \simeq 12R_c$, the factor $\exp(-\kappa_D r)$ is equal to $\simeq 10^{-19}$. In Fig. 15, as expected, the oscillations in all correlation functions have an identical period, although the numerical accuracy and short range contributions for $r \simeq 4 - 5R_c$ can preclude an exact coincidence of the oscillations which, however, is realized with an accuracy of $10^{-3}R_c$ for $r > 5R_c$.

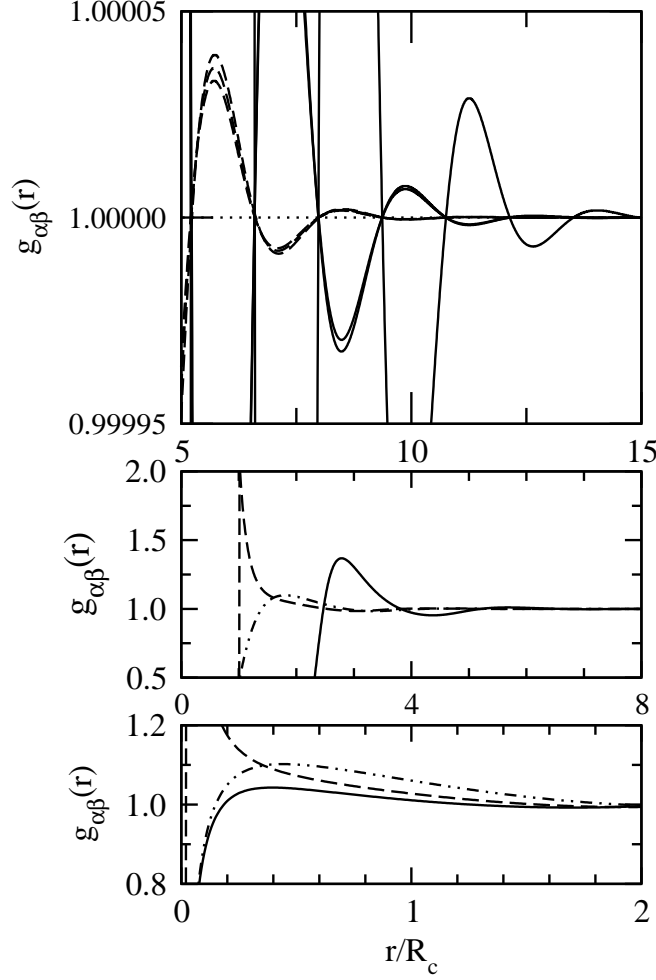


FIG. 15: At $\eta_c = 0.1$, $z_1 = -1$, $z_2 = 1$, $\rho_v = 0.003$ M and $z_0 = 108$, *bottom* : correlation functions $g_{11}(r)$ (solid line), $g_{12}(r)$ (dashed line) and $g_{22}(r)$ (dash-dotted line), *middle* : $g_{00}(r)$ (solid line), $g_{01}(r)$ (dashed line) and $g_{02}(r)$ (dash-dotted line), *top* : for $r > 5R_c$, close view showing the identity of the oscillation period of the six correlation functions, after an appropriate shift on r (cf. Fig. 11) of the ion-ion (dashed line) and colloid-ion (solid line) correlation functions, (notice that the maxima and minima of the oscillations of $g_{00}(r)$, $g_{01}(r)$ and $g_{02}(r)$ can be outside the limits of the figure).

Another example where the asymptotic behavior does not seem to be determined by the Debye screening, is found for $\eta_c = 0.001$, $z_0 = 300$, $z_1 = -1$, $z_2 = 1$ and $\rho_v = 0.001$ M. This conclusion is obtained from the fact that $g_{00}(r)$ is significantly larger than 10^{-6} for $r \simeq 10 - 12R_c$, a domain of r where $\exp(-\kappa_D r) \simeq 10^{-10}$ (cf. Table 1). For this suspension, the asymptotic behavior of the correlations seems well described by a superposition of two

exponentials ($k_p^0 = 0$, $k_o^0 = 0$) where $A_{\alpha\beta}^p$ and $A_{\alpha\beta}^o$ have opposite signs (cf. Fig. 12).

At $\eta_c = 0.0001$, $z_0 = 460$, $z_1 = -1$, $z_2 = 1$ and $\rho_v = 0.001\text{M}$, the asymptotic behavior is described by one exponential with a screening length κ_p compatible with the value of the Debye length, because the maximum of $g_{00}(r)$ exists at $r \simeq 8R_c$ where $\exp(-\kappa_D r) \simeq 10^{-7}$. However it is worth remarking that the signs of the $A_{\alpha\beta}^p$ coefficients for the colloid-colloid and ion-colloid functions are opposite to their expected values ; for instance A_{00}^p is positive (cf. Fig. 14). Clearly, this fact seems to preclude the interpretation of A_{00}^p in terms of an effective charge which implies $A_{00}^p \propto -Z_{eff}^2$ (cf. Eq. (9)).

For the considered suspensions, the OZ HNC equations predict that the asymptotic correlation of the two-body functions has several possible behaviors. For $z_0 > 100$, the decrease of these correlations at large r generally does not correspond to that induced by the Debye screening. Due to the large difference of size between colloids and ions, the colloid-colloid correlations, which have a range of several colloid diameters, determine at large r the behavior of all the correlations between the ions and the colloids and ions, as a consequence of the exact OZ relations. In particular, when z_0 increases, the excluded volume effects between the colloids are reinforced and $g_{00}(r)$ presents oscillations and looks like the pair correlation of a fluid of soft core particles at low or moderate densities.

IV. CONCLUSION

At the infinite dilution of the colloids, the ion-colloid pair correlation functions computed from the OZ HNC equations allows to define effective colloid-ion potentials and colloid-ion charges (Z_{eff}). The results obtained for ionic solutions where the ion density varies between 0.001M to 0.1M are in fair agreement with the effective potentials and charges obtained from PB theory when z_0 is smaller than 1000. For larger z_0 , the PB and HNC values of Z_{eff} differ. While the PB values go towards a constant value both for symmetric and asymmetric ionic solutions, the HNC values decrease and, in the case of the asymmetric solution $z_1 = -2$ and $z_2 = 1$, Z_{eff}^{HNC} becomes negative. This last result seems to be due to an overscreening of the colloid charge. The HNC theory shows that, when the ionic concentration is of the order of 0.1 M, the corrections to the Debye screening length due to finite density effects are not negligible in the computation of Z_{eff} . Although the difference between κ_p and κ_D is only 5%, it induces a factor of 3 on the value of Z_{eff} when in Eq. (12) κ_D is substituted to κ_p .

At finite concentrations of the colloids, all the correlation functions present an identical asymptotic qualitative behavior. The colloid-colloid correlations determine the decrease of this behavior. The analysis of the asymptotic behavior does not seem to allow, as in the case of infinite dilution, to define in a simple way a colloid-colloid effective potential or colloid effective charge from $v_{\alpha\beta}^m(r)$. The main reason is that, at large r , the colloid-colloid correlations, for large z_0 values may be dominated by excluded volume effects similar to those existing in fluids of particles interacting by a hard or soft core repulsive interaction. This result is in agreement with the fact that the range of the correlations is larger than that expected from the value of the Debye length controlling the charge screening. Obviously, it leaves open the possibility, largely discussed in the literature, to define an effective colloid-colloid potential, able to reproduce adequately both screening and excluded effects from a relation different from $\log\{g_{00}(r)\} = -\beta v_{00}^m(r)$ [36, 37, 38].

The HNC approximation has been proved reliable to describe the coulombic fluids by comparison with MC simulations. For the present model, such a test of the validity of HNC approximation seems prevented by the difficulty of realizing an efficient MC sampling of the configurations of colloid suspensions where the ratio of colloid and ion sizes is 80 and the colloid charges are much larger than 100. However, if the HNC approximation generally gives good quantitative results when it can be solved, the stability limit of the numerical solutions can not be faithfully associated with a thermodynamic transition. Thus, at the colloid packing fraction $\eta_c = 0.001$, the loss of stability of the numerical HNC solutions corresponding to the onset of a peak in $g_{00}(r)$ at $r \simeq 2.08$, cannot unambiguously be interpreted as the formation of colloid aggregates.

From the present results and those published in the literature [39, 40] it seems possible to extend the use of the HNC OZ equations for studying colloidal suspensions with colloid-ion size ratio larger than 80 and, also, to consider ionic solutions with a discrete solvent, at least for an infinite dilution of the colloids and to determine the influence of the solvent on the ion and solvent-colloid correlation functions and the values of Z_{eff} .

Acknowledgments

The authors are indebted to Jean-Michel Caillol and Emmanuel Trizac for helpful discussions.

- [1] E.J.W. Verwey and J. Th. G. Overbeek, *Theory of the Stability of Lyophobic Colloids* (Elsevier, Amsterdam, 1948).
- [2] J.P. Hansen and H. Löwen, *Annu. Rev. Phys. Chem.* 51, 209 (2000).
- [3] H. Löwen, E. Allahyarov, C.N. Lykos, R. Blaak, J. Dzubiella, A. Jusufi, N. Hoffmann and H.M. Harreis *Jour. Phys. A : Math. Gen.* 36, 5827 (2003).
- [4] B.V. Derjaguin and L. D. Landau, *Acta Physicochim. URSS* 14, 633 (1941).
- [5] A.A. Louis *Phil. Trans. Roy. Soc. A* 359, 939 (2001).
- [6] A.A. Louis, E. Allahyarov, H. Löwen and R. Roth *Phys. Rev. E* 65, 061407 (2002).
- [7] J.P. Hansen and I.R. McDonald, *Theory of Simple Liquids* (Academic, London, 1986).
- [8] L. Belloni *Chem. Phys.* 99, 43 (1985).
- [9] S. Khan, T. L. Morton and D. Ronis *Phys. Rev. A* 35, 4295 (1987).
- [10] V. V. Vlachy *J. Chem. Phys.* 99, 471 (1993).
- [11] D. Forciniti and C. K. Hall *J. Chem. Phys.* 100 7553 (1994).
- [12] L. Belloni *Coll. Surf, A* 140, 227 (1998).
- [13] S.K. Lai, J.L. Wang and G.F. Wang *J. Chem. Phys.* 110, 7433 (1999).
- [14] L. Belloni *J. Phys. Condens. Matter* 14 9323 (2002).
- [15] J.A. Anta and S. Lago *J. Chem. Phys.* 116, 10514 (2002).
- [16] G.M. Torrie, J.P. Valleau and G.N. Patey *J. Chem. Phys.* 4615 (1982).
- [17] M.C. Abramo, C. Caccamo, G. Malescio, G. Pizzimenti and S.A. Rogde *J. Chem. Phys.* 80, 4396 (1984).
- [18] C. Caccamo and G. Malescio *J. Chem. Phys.* 90, 1091 (1989).
- [19] R. Kjellander, T. Åkesson, B. Jönsson and S. Marcelja *J. Chem. Phys.* 95, 1424 (1992).
- [20] M. Bester and V. Vlachy *J. Chem. Phys.* 96, 7656 (1992).
- [21] Yu. V. Kalyuzhnyi, V. Vlachy, M.F. Holovko and G. Stell *J. Chem. Phys.* 102, 5770 (1995).
- [22] J. Ulander and R. Kjellander *J. Chem. Phys.* 114, 4893 (2001).

- [23] A. P. Lyubartsev and S. Marčelja Phys. Rev. E 65, 041202 (2002).
- [24] R. Kjellander and D.J. Mitchell J. Chem. Phys. 101, 603 (1994).
- [25] J. Ulander and R. Kjellander J. Chem. Phys. 109, 9508 (1998).
- [26] R. Evans, R.J.F. Leote de Carvalho, J.R. Henderson and D.C. Hoyle J. Chem. Phys. 100 591 (1994).
- [27] R.J.F. Leote de Carvalho, R. Evans and Y. Rosenfeld Phys. Rev. E 59 1435 (1999).
- [28] M. Dijkstra and R. Evans J. Chem. Phys. 112, 1449 (2000).
- [29] C. Tutschka and G. Kahl Phys. Rev. E 65, 051104 (2002).
- [30] C. Grodon, M. Dijkstra, R. Evans and R. Roth J. Chem. Phys. 121, 7869 (2004).
- [31] L. Bocquet, E. Trizac and M. Aubouy J. Chem. Phys. 117, 8138 (2002).
- [32] E. Trizac, L. Bocquet and M. Aubouy Phys. Rev. Lett. 89, 248301 (2002).
- [33] I.A. Shkel, O. V. Tsodikov and M. T. Record Jr. J. Phys. Chem. 104, 5161 (2000).
- [34] M. Aubouy, E. Trizac and L. Bocquet J. Phys. : Condens. Matt. 36, 5835 (2003).
- [35] G. Tellez and E. Trizac Phys. Rev. E 70, 011404 (2004).
- [36] T. Biben, On effective interactions in colloidal physics (page 359) in *New Approaches to Old and New Problems in Liquid State Theory* C, Caccamo (Editor), J.-P. Hansen, G. Stell, NATO Sciences Series, Kluwer Academic Publishers (1999)
- [37] J. Clément-Cottuz, S. Amokrane, and C. Regnaut Phys. Rev. E 61, 1692 (2000).
- [38] D. Gottwald, C.N. Likos, G. Kahl and H. Löwen Phys. Rev. Lett. 92, 068301 (2004).
- [39] P. G. Kusalik and G. N. Patey J. Chem. Phys. 88, 7715 (1988).
- [40] P. G. Kusalik and G. N. Patey J. Chem. Phys. 92, 1345 (1990).